Applied Geochemistry 125 (2021) 104860

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: http://www.elsevier.com/locate/apgeochem

Is the past history of acidic deposition in eastern Canada reflected in sugar maple's tree rings $^{87}Sr/^{86}Sr$, Sr and Ca concentrations?

D. Houle [a,b,*], C. Marty [c], C. Gagnon [a], S. Bilodeau Gauthier [b,d], N. Bélanger [e]

[a] Science and Technology Branch, Environment Canada and Climate Change, 105 McGill St., QC, H2Y 2E7, Montreal, Canada
[b] Direction de la Recherche Forestière, Ministère de la Forêt, de la Faune et des Parcs, 2700 rue Einstein, Sainte-Foy, Québec, G1P 3W8, Canada
[c] Carbone boréal, Département des sciences fondamentales, Université du Québec à Chicoutimi, 555 bd de l'université, G7H 2B1, Saguenay, Québec, Canada
[d] Centre d'étude de la forêt, Université du Québec à Montréal, 141 Président-Kennedy, Montréal, QC, H2X 1Y4, Canada
[e] Département science et technologie, Université TÉLUQ, 5800 rue Saint-Denis, bureau 1105, Montréal, Québec, H2S 3L5, Canada

ARTICLE INFO

Editorial handling by Prof. M. Kersten

Keywords:
Calcium
Strontium
$^{87}Sr/^{86}Sr$
Dendrochemistry
Temperate forests
Soil acidification
Sugar maple

ABSTRACT

How calcium (Ca) uptake by trees in eastern Canadian forests has responded to decades of atmospheric acid deposition and its sharp decrease that started three decades ago is still largely unknown. Here, we tested a novel approach based on the measurements of Ca and strontium (Sr) concentrations and Sr isotope signature ($^{87}Sr/^{86}Sr$ ratio) in sequential extracts of sugar maple tree rings and soils to assess changes in Ca availability and sources through time. The study was conducted at three sites showing a gradient of one order of magnitude in soil mineral weathering fluxes and exchangeable pools of Ca. We found that wood Ca and Sr concentrations increased with Ca and Sr concentrations in the exchangeable fraction (NH_4Cl extracts) of the top mineral soil across sites. In addition, wood $^{87}Sr/^{86}Sr$ ratio was strongly correlated with $^{87}Sr/^{86}Sr$ ratio of this soil fraction. Both Ca and Sr concentrations in the exchangeable fraction of the wood decreased from pith to bark at all sites, whereas no trend was observed for the wood residual fraction. This was interpreted as a result of radial mobility of Ca in sapwood rather than a decline in the uptake of Ca and Sr by tree roots over time. The $^{87}Sr/^{86}Sr$ ratio of tree rings slightly increased over time only at the site with the higher soil exchangeable Ca pool, suggesting an increase in the contribution of soil mineral weathering relative to atmospheric deposition. In contrast with our hypothesis, our results show i) no evidence of pronounced changes in the relative contribution of the atmospheric vs. soil mineral weathering Ca components over time at the site with the smallest soil exchangeable Ca pools; and ii) the difficulty of assessing the temporal changes in the availability and the sources of Ca from sequential extractions of the wood due to a dynamic exchange process of Sr (and therefore Ca) between the exchangeable and residual fractions of the wood.

1. Introduction

Decades of anthropogenic N and S depositions had detrimental impacts on terrestrial and aquatic ecosystems (Driscoll et al., 2001). The acidic anions in precipitation, mainly NO_3^- and SO_4^{2-}, contribute to the leaching of cations to surface waters due to charge balance effect (Galloway et al., 1983). This mechanism has resulted in the decrease of exchangeable base cations in forest soils in many regions of the world (Federer et al., 1989; Houle et al., 1997; Huntington 2000; Watmough 2018) and in forest dieback in regions with low buffering capacity and high acidic depositions (Duchesne et al., 2002; Hunova et al., 2004). Base cations such as Ca, K and Mg play important roles in forest ecosystems, being important nutrients for trees. Large base cations reservoirs in soils are also associated with higher soil pH and higher soil acid neutralizing capacity (Houle et al., 2006). Calcium is particularly important because it constitutes a large proportion of the base cation reservoir and is required in large amounts for tree nutrition (White and Broadley 2003; Marty et al., 2014). Primary sources of Ca for tree nutrition in forest ecosystems are atmospheric deposition and the weathering of Ca-bearing silicate and carbonate minerals (Clow et al., 1997). In sites where soils originate from felsic rocks (e.g. granite), plagioclase feldspars weathering is generally the main source of Ca released in soil and stream water, although the dissolution of carbonates, even at trace levels in the parental granitic rock, can constitute a large part of Ca exports due to its high solubility (Drever and Hurcomb 1986; Jacobson et al., 2002; Oliva et al., 2004; Bélanger et al., 2012;

* Corresponding author. Science and Technology Branch, Environment Canada and Climate Change, 105 McGill St., QC, H2Y 2E7 Montreal, Canada.
E-mail address: daniel.houle2@canada.ca (D. Houle).

https://doi.org/10.1016/j.apgeochem.2020.104860
Received 25 February 2020; Received in revised form 20 November 2020; Accepted 14 December 2020
Available online 1 January 2021

Augustin et al., 2016). The contributions from mineral weathering and atmospheric inputs to vegetation Ca requirements vary widely among sites. Atmospheric contribution tends to dominate at sites with highly weathered, old and Ca-poor geological substrate or at sites with high dust inputs (Kennedy et al., 1998; Perakis et al., 2006; Poszwa et al., 2009; Bélanger and Holmden 2010; Hynicka et al., 2016) and by mineral weathering at sites with Ca-rich bedrock or in tectonically active regions (Bailey et al., 1996; Vitousek et al., 1999; Bern et al., 2005; Bélanger et al., 2012; Hynicka et al., 2016). The long-term balance between these two sources can be regulated by environmental changes. Recently, a study conducted across 22 temperate forests in Oregon has shown that the contribution of the atmospheric Ca source increased with soil N enrichment at Ca-rich basaltic sites, resulting from the progressive depletion of the weatherable mineral Ca pool induced by N-rich soils (Hynicka et al., 2016).

Strontium (another alkaline earth element) has been often used as a proxy for Ca in environmental studies because both ions share similar valence and ionic radius (Capo et al., 1998). Consequently, Ca and Sr have similar dynamics in ecosystems and the contribution of different Ca sources can be investigated by analyzing the $^{87}Sr/^{86}Sr$ ratio in ecosystem compartments (Åberg 1995; Dambrine et al., 1997; Capo et al., 1998; Poszwa et al., 2000; Drouet et al., 2005b). Assuming that the chemical composition of tree rings reflects the chemical composition of soil solution, radial changes in Ca concentrations and $^{87}Sr/^{86}Sr$ are thought to be indicative of changes in the size of soil Ca exchangeable pools and Ca sources, respectively. For instance, using long-term temporal changes in wood Sr isotopic signature, Drouet et al. (2005a) found an increase in the atmospheric source contribution in European forests, which was ascribed to shrinking soil Ca exchangeable pools resulting from increased SO_4 deposition. In North America, changes in wood Sr isotopic signature was suggested to be the result of progressive shallowing of the effective depth of nutrient uptake by roots due to acidification of the mineral soil and subsequent toxic Al levels (Bullen and Bailey 2005). However, several studies have since shown that there is a "natural" decrease in Ca concentration from heartwood to the bark that results from radial re-equilibration, i.e. the radial mobility of Ca in sapwood, and to the increasing number of pectate binding sites with tree ring age, which can be erroneously ascribed to changes in soil Ca availability over time (Momoshima and Bondietti 1990; Herbauts et al., 2002). The same mechanism probably applies to Sr. For example, a change in soil $^{87}Sr/^{86}Sr$ induced by liming was detected in total digestion of tree rings about 50 years prior to lime application due to element mobility in sapwood (Drouet et al., 2005a). The bias caused by radial re-equilibration may be potentially avoided by using sequential extractions. Although they are widely used in environmental studies for soils and lake sediments, sequential extractions are seldom used in tree ring research. Sequential extractions with H_2O, 0.05N HCl and 1N HNO_3 were previously conducted on sugar maple sapwood to distinguish soluble, exchangeable and residual fractions, respectively (Bilodeau--Gauthier et al., 2008). Most of wood Ca was found in the soluble and exchangeable fractions, suggesting high radial mobility for Ca. Consequently, radial changes in total Ca concentration in tree rings may not be the best proxy to detect long-term changes in soil Ca availability. In contrast, the residual fraction of Ca in wood could be a more robust indicator of changes in soil chemistry over time, on the basis that radial re-equilibration mechanisms presumably affect the exchangeable fraction alone (Bilodeau Gauthier et al., 2008). Although Sr and Ca have similar dynamics in plant tissues, much less is known in regard to Sr radial mobility in the wood and Sr distribution among the different fractions. To our knowledge, whether exchangeable and residual fractions of tree rings exhibit different $^{87}Sr/^{86}Sr$ signatures has also never been documented.

In the present study, we measured Ca and Sr concentrations, as well as $^{87}Sr/^{86}Sr$ after sequential extractions of tree rings and soils sampled at three sugar maple forests of southern Quebec, Canada. These sites are characterized by contrasted weathering rates (Houle et al., 2012; Augustin et al., 2015) and soil base cation exchangeable reservoir that vary by one order of magnitude (Bilodeau-Gauthier et al., 2011). One of these sites, Duchesnay, has been strongly impacted by atmospheric acid deposition, resulting in net Ca losses of soil exchangeable pools (Houle et al., 1997) and large decreases in tree growth (Duchesne et al. 2002, 2003). The goals of this study were to assess whether the changes in Ca availability can be detected through the analysis of Ca and Sr concentrations and Sr isotopic composition in the exchangeable and residual wood fractions. We hypothesized that 1) the wood residual fraction is a better proxy of past changes in Ca availability than total wood Ca and Sr concentrations; 2) the rate of decrease in Ca concentration in the wood residual fraction is stronger at the most severely Ca-depleted sites; and 3) changes in the $^{87}Sr/^{86}Sr$ signature of tree rings reflect past changes in the relative contribution of weathering and atmospheric deposition to Ca tree uptake. If so, we hypothesized that the most Ca-impoverished sites would show the largest changes.

2. Material and methods

2.1. Study sites

Wood and soil samples were collected in three forested watersheds (Fig. 1) of the Quebec Lakes Network (Houle et al., 2006; Marty et al., 2015). Despite being all dominated by sugar maple (Acer saccharum), the three sites provided a large gradient in soil acidity (i.e., pH, base saturation, Ca/Al ratio, exchangeable acidity) and in the rate of Ca mineral weathering (Duchesnay < Truite Rouge < Blais) (Table 1) (Bilodeau-Gauthier et al., 2011). The contrasting rate of Ca weathering among sites is explained by the soil calcite content which vary from 2, 0.5 and 0 percent for Blais, Truite Rouge and Duchesnay, respectively (Houle et al., 2012; Ouimet and Duchesne, 2005). Soils at the sites are classified as Orthic Ferro-Humic or Humo-Ferric Podzols or Eluviated Dystric Brunisols, with a mor or moder humus type (Soil Classification Working Group, 1998).

2.2. Soil sampling and sequential extractions

Soil sampling and laboratory extractions were conducted as described in Bilodeau-Gauthier et al. (2011). Four soil samples were taken at ~2.5 m from the base of the tree at each major cardinal point. Mineral soil (first 15 cm of the B horizon) were sampled separately and then pooled by horizon type. Soil samples were air-dried, ground and sieved to 2 mm. The exchangeable fraction of the mineral soil was extracted using an unbuffered NH_4Cl[1N] solution, which serves as a proxy for exchangeable cations, followed by HNO_3[1N], HNO_3[15N] and concentrated HF digests as described by Bélanger and Holmden (2010) and Holmden and Bélanger (2010): 1) 30 ml of NH_4Cl[1N] solution were added to the soil sample in a 50 ml trace metal-cleaned centrifuge tube on a shaker for 2 h at room temperature; 2) the sample was rinsed and decanted several times with ultrapure water to remove excess NH_4Cl and then subjected to a weak acid leach using 30 ml HNO_3[1N] at room temperature for 2 h; 3) the supernatant was removed by centrifugation and the residue treated with 30 ml of HNO_3[1N] for 8 h at 80 °C; and 4) a 150 mg aliquot of the residue was acid digested in a 2.5:1 mixture of concentrated HF–HNO_3 at ~120 °C for 48 h, and then refluxed in HCl[6N] several times after dissolution to remove fluorides. The 1N–NH_4Cl is thought to extract Ca and Sr from the soil exchangeable complex. The HNO_3[1N] is thought to remove Ca and Sr from the crystal lattice of calcite and apatite and possibly some Ca and Sr from phyllosilicates, hornblende and epidote (Nezat et al., 2007). The HNO_3[15N] digest attacks phyllosilicates, hornblende and other more resistant minerals (e.g. K-feldspars). The final HF–HNO_3 dissolves the remaining minerals such as K-feldspars, plagioclase and quartz. Only the mineral soil was analyzed for Sr isotopes given that we were interested in the different mineral fractions and in the source of mineral weathering for base cations. A previous study conducted in 17 sugar maple

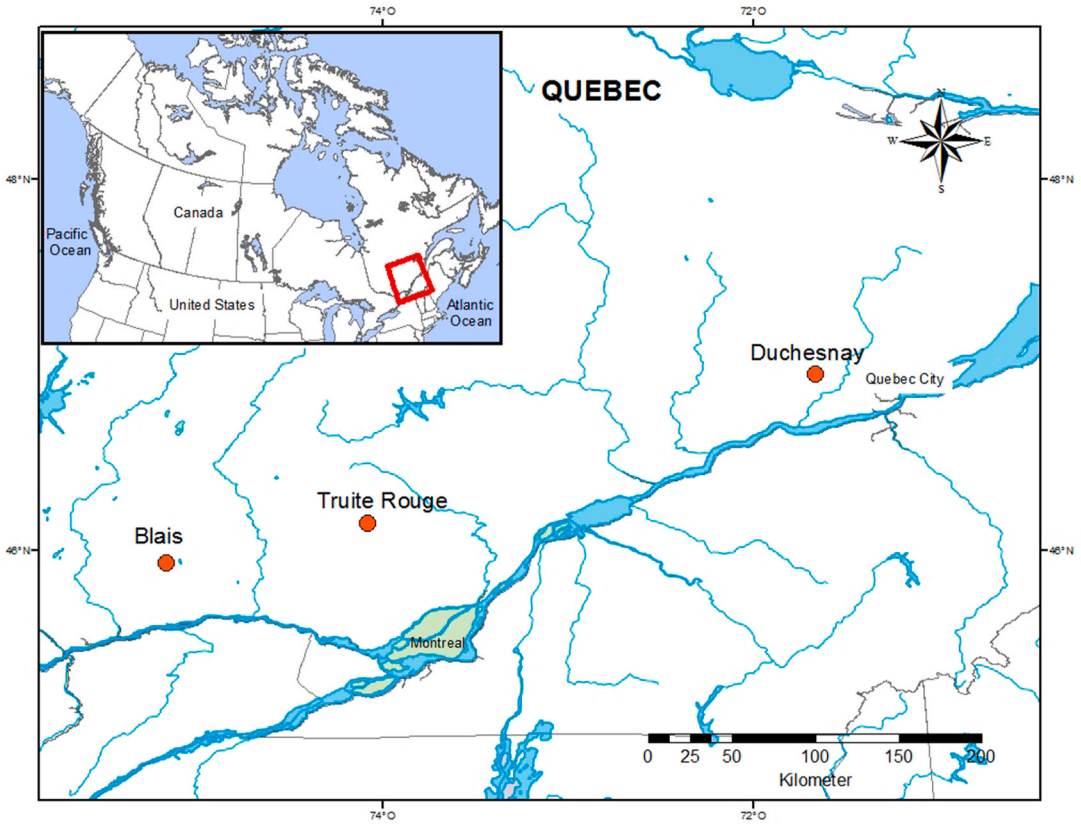

Fig. 1. Location of the three study sites (Québec, Canada).

Table 1
Table 1 Characteristics of the upper mineral soil horizon (first 15 cm of B) for the three sites. * data from Bilodeau-Gauthier et al. (2011); † data from Houle et al. (1997); ‡ data from Houle et al. (2012). EA: Exchangeable acidity; CEC: Cation exchange capacity; BS: Base saturation.

	Sites		
	Duchesnay	Truite Rouge	Blais
Latitude	46°57′ N	46°09′ N	45°56′ N
Longitude	71°40′ W	74°05′ W	75°10′ W
pH ($cmol_c\ kg^{-1}$)*	4.6	4.8	5.1
Ca ($cmol_c\ kg^{-1}$)*	0.3 (0.09)	0.6 (0.3)	5 (4)
Ca/Al*	0.05	0.21	3.76
EA ($cmol_c\ kg^{-1}$)*	5.6	3.1	1.6
CEC ($cmol_c\ kg^{-1}$)*	6 (1)	4 (1)	7 (3)
BS (%)*	10 (2)	21 (10)	74 (21)
Ca mineral weathering rate ($kg\ ha^{-1}\ yr^{-1}$)	2.4†	12.3‡	55.1‡
Ca atmospheric deposition ($kg\ ha^{-1}\ yr^{-1}$)	2†	3.4‡	2.7‡

stands in Quebec showed that the chemistry of the top B horizon was more reliable than the organic horizon for predicting variations in wood and foliage chemistry among sites (Houle et al., 2007).

2.3. Wood sampling and sequential extractions

Analyses were performed on wood samples collected at the sites during 2004 and 2005 as reported by Bilodeau-Gauthier et al. (2008). Eight to fourteen tree trunks were sawed at breast height and a 10 cm thick section was taken to the laboratory. Three trees were then randomly selected from each site for the sequential chemical extractions. Tree rings were separated and analyzed by 5-years groups. The position of the heartwood–sapwood boundary on the tree cores was determined visually based on wood color differences. Very small wood chips (0.2 mm) were prepared with a ceramic knife to increase the contact surfaces of the wood samples during the extraction process. The tree ring samples were then dried in a desiccator at 30 °C until constant weight was reached.

Sequential chemical extractions of wood samples were performed with HCl[0.05N] (exchangeable fraction) followed by a digestion with HNO_3[15N] (residual fraction) as described in Bilodeau-Gauthier et al. (2008). For the first extraction, 30 ml of HCl[0.05N] was added to 3 g of ground wood and agitated at 30 rpm for 2 h, followed by centrifugation. The supernatant was fixed until analysis. The remaining wood was rinsed with deionized water and then dried for 48 h at 70 °C. For the second extraction, 300 mg of wood was taken from the 3 g remaining from the first extraction. Wood samples were put in Teflon bombs (CEM linear closed-vessels) with 3 ml of ultrapure concentrated HNO_3 and digested in a high-performance microwave (MDS-2000, from CEM corp.). The digested solutions were transferred to polyethylene tubes and the volume adjusted to 30 ml with deionized water.

2.4. Elemental analyses in soil and wood samples

Calcium and Sr analyses were done on a charge coupled device simultaneous inductively-coupled plasma atomic emission spectrometer (CCD simultaneous ICP-AES) equipped with an axial torch (model Vista AX from Varian, Australia, 1999). Replicability of the extraction method was verified with a series of 10 ground wood samples, obtained by subsampling from a homogenous combination of 20 annual rings from the sapwood of a single tree. These 10 samples were treated with the above-described extraction method.

2.5. Isotopic analyses of soil and wood samples

All $^{87}Sr/^{86}Sr$ analyses were performed by thermo-ionization mass spectrometry (TI-MS; MAT 261-Finnigan). Prior to $^{87}Sr/^{86}Sr$ analysis, Sr was separated on columns containing 150 μL of cation exchange resin (Sr-SPEC, 200–400 mesh, Eichrom Technologies LLC, IL, USA). The volume of the sample solution was determined so that at least 300 ng of Sr would be contained in the analyzed solution. Two purification phases were performed successively with 2N and 7N HNO_3 solutions. Strontium elution was done with a 0.05N HNO_3 solution. The eluate was then collected and evaporated, and the remaining solid fraction was dissolved in a mix of 0.02N H_3PO_4 and 1N HCl for analysis. The measured $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$. The accuracy of the measurements was checked against the NBS-987 standard. The average value (0.710242 ± 0.000015; 2σ, n = 12) fell within the range of the standard, which means that no instrumental bias needed to be considered.

2.6. Mixing equation

The following mixing equation was used to estimate the contributions of soil mineral weathering and atmospheric sources to the soil exchangeable fractions (NH_4Cl extract):

$$\beta(Ca) = \frac{(Sr/Ca)_{mw} \times [X_{mw} - X_{exch}]}{(Sr/Ca)_{atm} \times [X_{exch} - X_{atm}] + (Sr/Ca)_{mw} \times [X_{mw} - X_{exch}]}$$

where ß(Ca) is the proportion of Ca in the soil exchangeable fraction (exch) originating from soil mineral weathering (mw); X_{exch}, X_{mw} and X_{atm} the $^{87}Sr/^{86}Sr$ ratios of the soil exchangeable fraction (exch), mineral weathering (mw) and atmospheric deposition (atm), respectively; and $(Sr/Ca)_{atm}$ and $(Sr/Ca)_{mw}$, the Sr/Ca ratios of atmospheric deposition and mineral weathering, respectively. The $^{87}Sr/^{86}Sr$ and Sr/Ca ratios of the HNO_3[1N] soil fraction were used as a proxy of the soil mineral weathering end-member. Given the proximity of the three sites, we assumed the $^{87}Sr/^{86}Sr$ ratio of atmospheric deposition was similar at the three sites. Simonetti et al. (2000) reported $^{87}Sr/^{86}Sr$ ratios of 0.71023, 0.71002 and 0.71043 for snow collected at sites located in the vicinity of Duchesnay, Truite Rouge and Blais, respectively [plots 21, 3 and 23 in Simonetti et al. (2000)]. Bélanger et al. (2012) reported an average $^{87}Sr/^{86}Sr$ of 0.71036 for bulk deposition at a site in the Laurentians, just north of Montreal, which is within the study area and approximately 30 km from the Truite Rouge site. We used a Sr/Ca value of 1/555 for the atmospheric end-member (Bélanger et al., 2012). All end-members used in the equation are listed in Table 3. The calculation was not made for the Blais site because the isotopic composition values of the exchangeable fraction and mineral weathering products were too close to each other (Table 3, Figure S1).

2.7. Statistical analyses

Normality of data was tested with the Shapiro-Wilk test. Analyses of variance (ANOVA) were performed to test the effect of site, extractants and their interaction on both soil and wood $^{87}Sr/^{86}Sr$, Ca and Sr concentrations. Calcium and Sr concentrations in heartwood and sapwood were compared with a *t*-test for each site. When the number of values was too low or data were not normally distributed, a Wilcoxon rank sum test was performed instead. Significance of long-term trends in Sr and Ca concentrations, and $^{87}Sr/^{86}Sr$ in tree rings were assessed with a Mann-Kendall test using the Kendall function from the library Kendall in R 3.6.2 (R Development Core Team, 2015). When a statistically significant trend was detected by the Mann–Kendall test, the Sen slope was calculated using the zyp. sen function from the "zyp" library in R.

3. Results

3.1. Soil Ca and Sr concentrations and $^{87}Sr/^{86}Sr$

Both Ca and Sr concentrations were several orders of magnitude lower in the NH_4Cl extract (i.e. the exchangeable fraction) than in the HF extract at all sites (Fig 2A and B). Concentrations in the NH_4Cl extract significantly increased from Duchesnay (3.1 ± 1.0 mg Ca kg^{-1}; 0.04 ± 0.02 mg Sr kg^{-1}) to Truite Rouge (9.7 ± 4.6 mg Ca kg^{-1}; 0.09 ± 0.04 mg Sr kg^{-1}) to Blais (32.1 ± 29.2 mg Ca kg^{-1}; 0.31 ± 0.28 mg Sr kg^{-1}). There were no significant differences among sites for the other extracts (Table S1).

There was a significant effect of the sites and the extractants on soil $^{87}Sr/^{86}Sr$ ratio (Table S2). Fig. 2C shows the variations in the $^{87}Sr/^{86}Sr$ ratio among extracts and sites. The most insightful results are that: i) the $^{87}Sr/^{86}Sr$ ratio tended to be lower in the NH_4Cl extract (particularly at Truite Rouge) and the highest in the HNO_3[15N] extract at all sites; ii) the $^{87}Sr/^{86}Sr$ ratios in the NH_4Cl extract decreased in the following order: Duchesnay (0.7139 ± 0.0003) > Blais (0.7112 ± 0.0015) >Truite Rouge (0.7105 ± 0.0005) (Fig. 2C); iii) the HNO_3[15N] extract at Duchesnay had a much higher $^{87}Sr/^{86}Sr$ ratio (0.7498 ± 0.0367) than the other fractions at the three sites. The $^{87}Sr/^{86}Sr$ in the HF fraction decreased from Duchesnay (0.7197 ± 0.0006) to Truite Rouge (0.7173 ± 0.0013) to Blais (0.7114 ± 0.0005).

3.2. Wood Ca and Sr concentrations and $^{87}Sr/^{86}Sr$

Wood total Ca concentration (the sum of exchangeable and residual fractions) increased from Duchesnay (706.0 ± 719.7 μg g^{-1}) to Truite Rouge (972.0 ± 460.4 μg g^{-1}) to Blais (1288.0 ± 1347.4 μg g^{-1}) (Fig. 2A). Wood total Sr concentration was significantly higher at Blais (17.2 ± 14.4 μg g^{-1}) than at the two other sites (8.0 ± 5.3 μg g^{-1} and 5.9 ± 4.6 μg g^{-1} at Duchesnay and Truite Rouge, respectively) (Fig. 2B). Wood $^{87}Sr/^{86}Sr$ ratios were similar to those in soil's NH_4Cl extract and decreased in the following order: Duchesnay (0.7135 ± 0.0004) > Blais (0.7108 ± 0.0012) > Truite Rouge (0.7101 ± 0.0004) (Fig. 2C).

3.3. Trends in tree rings Ca and Sr concentrations

Ca and Sr concentrations were much higher in the heartwood than in the sapwood for both the exchangeable and residual fractions, particularly in the oldest tree rings (Fig. 3). Both Ca and Sr concentrations in the exchangeable fraction significantly decreased over time (Table 2). The decrease was however much less pronounced in the sapwood, especially for the residual fraction, for which a significant trend was detected only for one tree at Truite Rouge and at Blais (Table 2).

3.4. Comparison of $^{87}Sr/^{86}Sr$ ratios between wood exchangeable and residual fractions

In a first step, a subset of wood tree ring samples from the three sites (n = 32: 14 from Duchesnay and 9 from Truite Rouge and Blais) was used to test if there was a difference between the exchangeable (HCl [0.05N]) and residual (HNO_3[15N]) fractions of wood $^{87}Sr/^{86}Sr$. At all sites, wood $^{87}Sr/^{86}Sr$ ratios of both fractions were strongly correlated (Fig. 4) and close to the 1:1 line (average values were not significantly different, Table S3). Consequently, further measurements of $^{87}Sr/^{86}Sr$ in tree rings were done only for the exchangeable fraction.

3.5. Trends in $^{87}Sr/^{86}Sr$ ratios in tree rings

Tree rings $^{87}Sr/^{86}Sr$ ratios slightly but significantly increased (Mann-Kendall test; $P < 0.01$) between 1910 and 2007 for the three sampled trees at Blais (Fig. 5c), whereas it decreased in the heartwood (from 1925 to 1960) and then increased in the sapwood (from 1960 to 2007) at Duchesnay in only one tree (Fig. 5a). There was no significant trend for

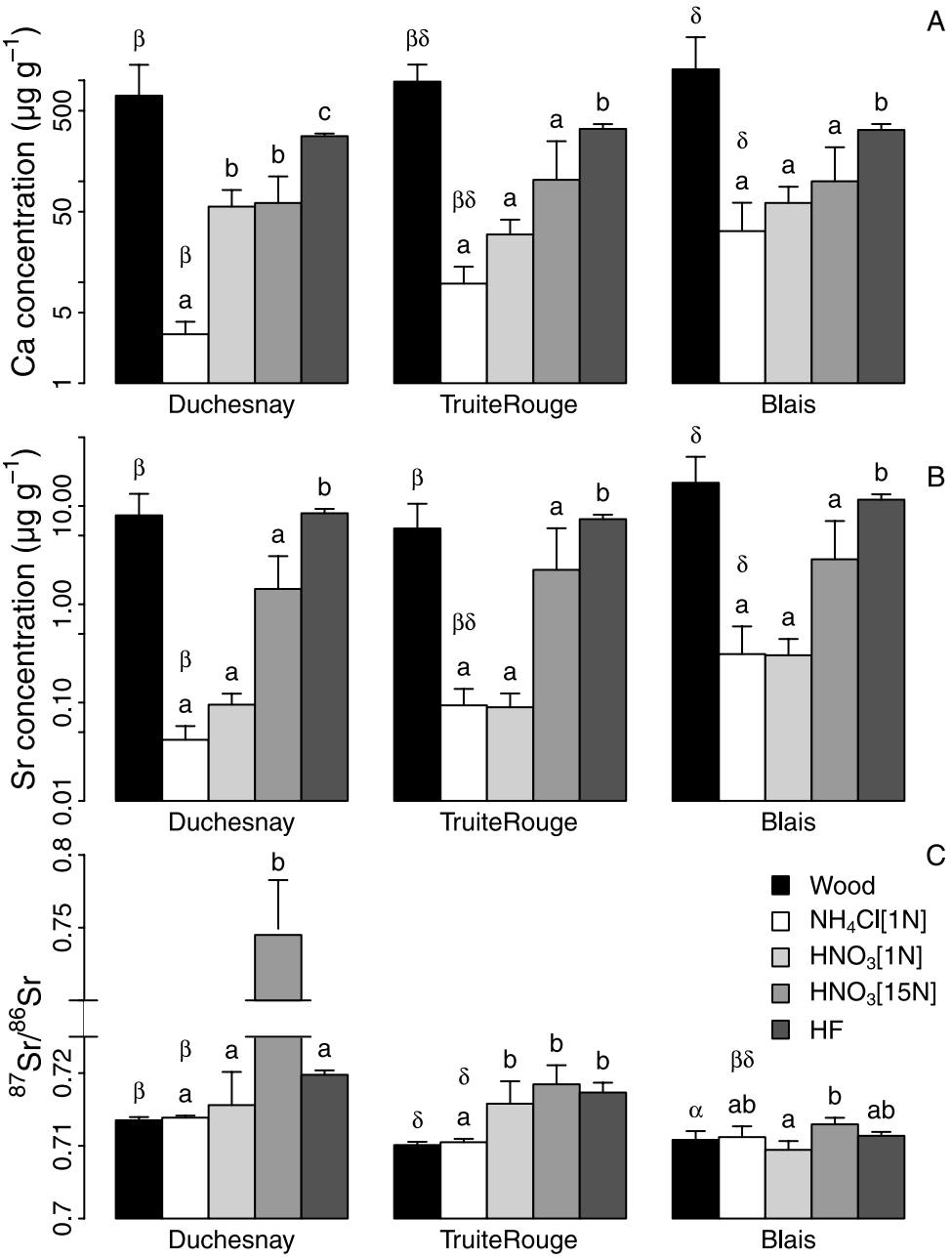

Fig. 2. Mean Ca and Sr concentrations (µg g^{-1}), and $^{87}Sr/^{86}Sr$ values in the wood exchangeable fraction and the different soil extracts (NH_4Cl[1N], HNO_3[1N], HNO_3[15N] and HF) at the Duchesnay, Truite-Rouge and Blais sites. Note the logarithmic scales in panels A and B. Roman letters show the difference among soil extracts within each site. Greek letters show the difference among sites for concentrations and isotopic ratios in the wood and soil's NH_4Cl[1N] extract. Values not sharing the same letter are significantly different ($P < 0.05$; ANOVA followed by Tukey's HSD test).

the three sampled trees at Truite Rouge (Fig. 5b).

3.6. Relationship between $^{87}Sr/^{86}Sr$ in wood and in the soil exchangeable fraction

There was a very strong positive correlation between $^{87}Sr/^{86}Sr$ ratios in the wood and in the soil exchangeable fraction (NH_4Cl[1N] extract) (Fig. 6). The ratio was slightly lower in the wood than in the soil fraction at all sites. Wood $^{87}Sr/^{86}Sr$ at Truite Rouge was close to the average $^{87}Sr/^{86}Sr$ in total precipitation (0.71036) reported by Bélanger et al. (2012) and the range in snow precipitation $^{87}Sr/^{86}Sr$ (0.71002–0.71043) reported by Simonetti et al. (2000) for the region, whereas both soil (NH_4Cl[1N] extract) and wood $^{87}Sr/^{86}Sr$ at Blais were slightly higher. In contrast, both the soil exchangeable pool and wood $^{87}Sr/^{86}Sr$ at Duchesnay were much higher (>0.7135).

4. Discussion

Decades of acidic deposition have resulted in the loss of base cation availability on soils developed from felsic rocks, which in some cases led to decreases in tree growth notably in the sugar maple forests of eastern Canada (Houle et al., 1997; Duchesne et al., 2002). Changes in Ca concentrations and $^{87}Sr/^{86}Sr$ ratio in tree rings have been used to track changes in the availability and sources of Ca over time due to ecosystem acidification (Drouet et al., 2005a) but this method can be biased by radial movements of Ca and Sr in tree rings (Bondietti et al., 1989; Momoshima and Bondietti 1990). We hypothesized that this bias could be alleviated by using sequential extractions and using the less mobile residual fraction of wood Ca and Sr. We also hypothesized that changes in both Ca concentrations and $^{87}Sr/^{86}Sr$ ratio in this residual fraction would be more pronounced at sites with low soil Ca availability and weathering rates due to a stronger reliance upon the atmospheric source.

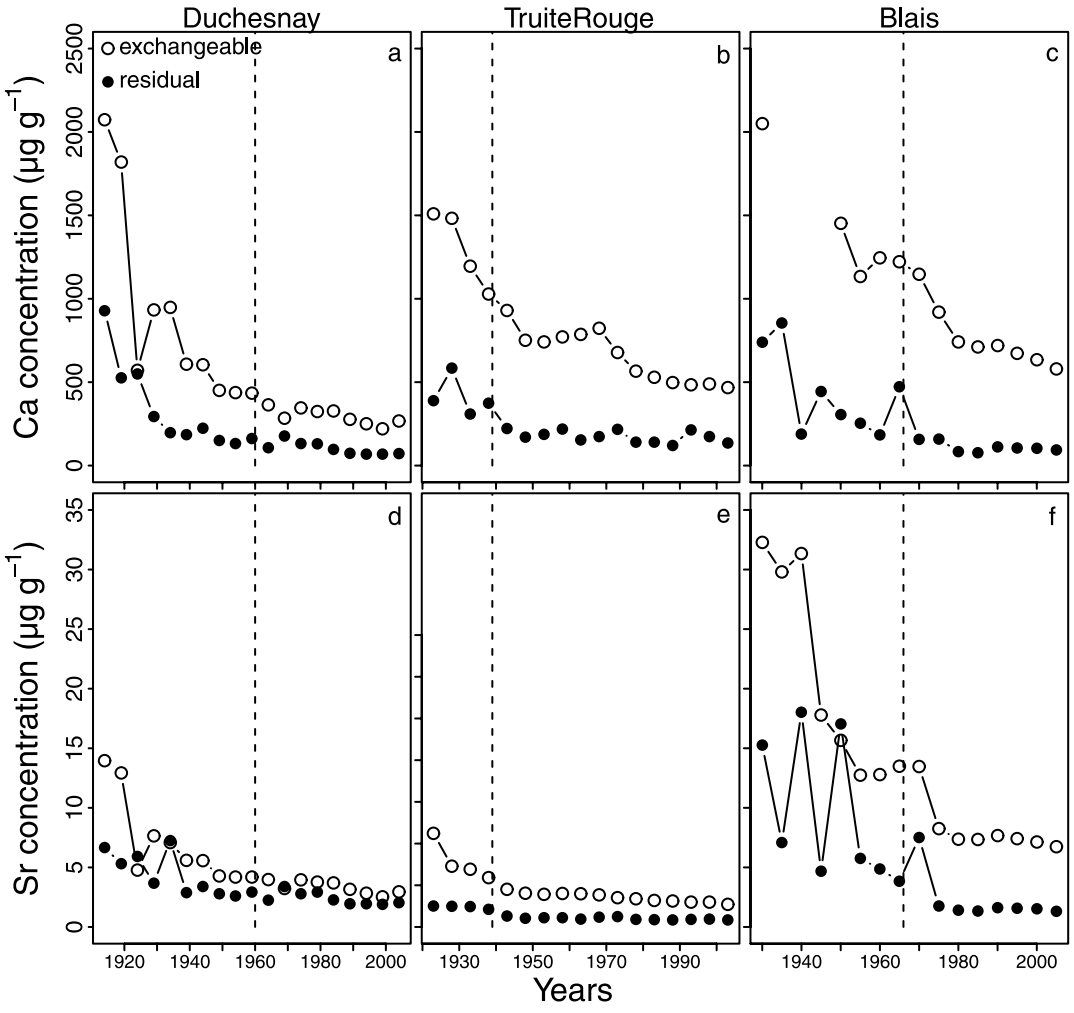

Fig. 3. Mean Ca (µg g^{-1}) and Sr concentrations (µg g^{-1}) in tree rings at the Duchesnay (a, d), Truite Rouge (b, e) and Blais (c, f) sites. Values are shown for the two sequential extractions with HCl[0.05N] (i.e. exchangeable fraction; open circles) and HNO_3 [15N] (i.e. residual fraction; closed circles). Each value is the mean of three sampled trees. Standard deviation values are not shown for clarity. Dotted lines show the delimitation between heartwood and sapwood.

Table 2
Trends in Ca and Sr concentrations in the exchangeable (HCl extract) and the residual (HNO_3 extract) fractions of sapwood at the Duchesnay, Truite Rouge and Blais sites. Values indicate the Sen's slope. Mann-Kendall test was performed. Significant trends are notified. ns: not significant; *p < 0.05; ** p < 0.01; *** p < 0.005.

		Exchangeable fraction		Residual fraction	
Sites	Tree	Ca	Sr	Ca	Sr
Duchesnay					
	1	−0.722***	−0.866*	−0.389 ns	−0.111 ns
	2	−0.167 ns	−0.055 ns	0.056 ns	0.222 ns
	3	−0.891***	−0.927***	−0.455 ns	−0.345 ns
Truite Rouge					
	1	−0.846***	−0.872***	−0.256 ns	−0.462*
	2	−1***	−0.810*	0.429 ns	0.047 ns
	3	−0.857***	−0.857***	−0.429 ns	−0.286 ns
Blais					
	1	−0.905***	−0.571***	−0.048 ns	−0.214 ns
	2	−0.964***	−0.745***	−0.564*	−0.527*
	3	−0.857***	−0.778***	−0.389 ns	−0.444 ns

4.1. The soil NH_4Cl extract reflects wood Ca and Sr composition

The Ca and Sr concentrations in the NH_4Cl extract of the top mineral soil differed among sites, which agrees with the difference in Ca and Sr fluxes originating from the soil weathering components reported in previous studies (Houle et al. 1997, 2012). The differences among sites in both Ca and Sr concentrations and in $^{87}Sr/^{86}Sr$ ratio in the soil NH_4Cl extracts were reflected in wood, confirming that this soil extract is a good proxy for Ca availability and sources at the study sites. This result agrees with the data of Houle et al. (2007) that showed that top mineral soil chemistry was the best predictor (better than the organic horizon chemistry) of both wood and foliage chemistry along a large base saturation gradient including 17 sites in Quebec. Other studies have found that deep horizons (up to 2.5 m) may represent a substantial source of Ca for trees (Drouet et al., 2015; Bedel et al., 2016), but this is unlikely at our sites given the superficial rooting of sugar maple (Houle et al., 2007; Chen et al., 2013). The similarity between the $^{87}Sr/^{86}Sr$ ratio in the wood and in the soil NH_4Cl fraction may also partly result from efficient recycling of Sr and Ca inputs from the litter, which can be released to the upper mineral soil and rapidly taken up by trees as shown at Ca-poor forest sites in northern Europe (van der Heijden et al. 2013, 2014). The higher $^{87}Sr/^{86}Sr$ ratio in both the wood and the soil NH_4Cl fraction at Duchesnay probably resulted from the slow release of Sr from

Table 3
Values used in mixing equation (equation 1) to estimate relative contribution of atmospheric deposition vs. mineral weathering to soil Ca exchangeable pool. X_{ech}, X_{mw} and X_{atm} are $^{87}Sr/^{86}Sr$ values in soil exchangeable fraction (ech), of mineral weathering (mw) and atmospheric deposition (atm), respectively. Soil 1N HNO_3 extract was used as a proxy for mineral weathering output.

	Duchesnay	Truite Rouge	Blais	Source
X_{ech}	0.7139	0.7105	0.7112	NH_4Cl extract
X_{mw}	0.7156	0.7158	0.7094	1N HNO_3 extract
Sr/Ca_{mw}	1/1254	1/725	1/438	1N HNO_3 extract
X_{atm}	0.71002–0.71043			Simonetti et al. (2000); Bélanger et al. (2012)
Sr/Ca_{atm}	1/555			Bélanger et al. (2012)

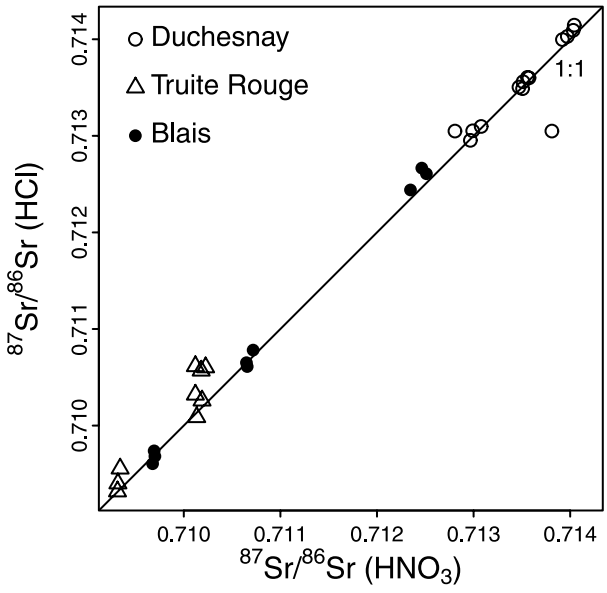

Fig. 4. Wood $^{87}Sr/^{86}Sr$ ratios in the exchangeable (HCl[0.05N]) vs. residual (HNO_3[15N]) fractions at the Duchesnay (n = 14), Truite Rouge (n = 9) and Blais (n = 9) sites.

minerals characterized by $^{87}Sr/^{86}Sr$ ratio higher than 0.75, as suggested by the soil HNO_3[15N] extracts in our study. Such minerals include biotite, garnet, muscovite as well as some minerals of the plagioclase and feldspar series (Hajj et al., 2017). The Duchesnay site has higher plagioclase and muscovite contents than the two other sites but a lower biotite content (Houle et al., 2012, Ouimet and Duchesne, 2005). It thus remains unclear which precise mineral was responsible for the high $^{87}Sr/^{86}Sr$ ratio in the HNO_3[15N] extract at Duchesnay.

4.2. *Can changes in the availability and the sources of Ca be inferred from tree rings?*

Despite the covariation of Ca concentrations and $^{87}Sr/^{86}Sr$ ratio in wood and the soil NH_4Cl fraction among sites, our data show that the inference of changes in long-term Ca availability from tree rings may not be possible. Given the reported decrease in Ca availability at the Duchesnay site in the past decades (Houle et al., 1997; Duchesnay et al., 2002), we expected a corresponding decline in the residual Ca concentrations of the wood during the same period. However, our results show that tree rings Ca and Sr concentrations only varied in the exchangeable fraction of the wood (representing 73–86% and 58–80% of total wood Ca and Sr, respectively). As reported in other studies, this outward decrease may result from radial re-equilibration and decreasing density of binding sites from the heartwood to the bark (Bondietti et al., 1989; Herbauts et al., 2002; Houle et al., 2002; Drouet et al., 2005a) rather than from a decrease in Ca root uptake over time. In contrast, the absence of a decreasing trend in Ca and Sr concentrations in the wood residual fraction indicates that either no change in Ca availability occurred or that this fraction is also not a good indicator of changes in soil Ca availability over time. Whatever the reason, it invalidates our hypothesis that Ca concentrations in the wood residual fraction would decrease, at least at the more Ca-poor site (Duchesnay), as a result of decreasing Ca availability due to decades of high acidic deposition. This observation and the fact that similar rates of decline were observed in the exchangeable fraction of the wood at the three study sites, over a gradient of soil Ca availability of one order of magnitude, reinforce the idea of a phenomenon inherent to wood properties rather than to potential changes in soil Ca and Sr availability over time.

While the assessment of Ca and Sr concentrations in the wood fractions failed to identify potential changes in soil Ca availability over time, the changes in Ca sources can be potentially inferred from temporal change in $^{87}Sr/^{86}Sr$ tree rings (Bullen and Bailey 2005; Drouet et al., 2005a), assuming that the isotopic signature of mineral weathering and atmospheric deposition are substantially different. Such an inference was not possible at Blais because the $^{87}Sr/^{86}Sr$ of the soil mineral weathering component (HNO_3[1N] fraction) was slightly lower than that of the soil NH_4Cl extract (exchangeable fraction), which yielded incoherent results (negative contribution). Nevertheless, this result suggests a strong contribution of the weathering products to the soil Ca exchangeable pool and corroborates with the very high Ca weathering rate (55.1 kg ha^{-1} yr^{-1}) relative to atmospheric deposition Ca flux (2.7 kg ha^{-1} yr^{-1}) at the site (Table 1).

The result of the mixing equation (eqn 1) for the Truite Rouge and Duchesnay sites indicated that, in contrast with our expectations, the contribution of soil mineral weathering to the exchangeable Ca pool was much lower at Truite rouge (17%) than at Duchesnay (83%) despite that the mineral weathering Ca flux is five times higher at Truite Rouge (12.3 kg ha^{-1} yr^{-1}) than at Duchesnay (2.3 kg ha^{-1} yr^{-1}) with nearly similar atmospheric deposition Ca fluxes (Table 1). The reasons for such a discrepancy cannot be elucidated from the present data. However, this estimation may be biased at Duchesnay. Indeed, the soil HNO_3[15N] extract at this site was characterized by a particularly high $^{87}Sr/^{86}Sr$ ratio (~0.75). Although we assumed that this fraction of soil Ca is not available for tree uptake, previous studies have shown the existence of active mycorrhizal weathering of soil minerals (Blum et al., 2002; van Schöll et al., 2006), which could provide trees with access to Ca and Sr sources from minerals that are generally considered recalcitrant to weathering and thus unavailable to plants. Indeed, if the trees at Duchesnay partly feed from the soil HNO_3[15N] fraction, this would artificially raise the estimated contribution of weathering calculated with the mixing equation. Part of the discrepancy between the two sites could also be due to differences in retention of atmospherically-derived Ca. Isotopic tracing has shown very high retention of throughfall-derived Ca in the soil (close to 100%) in beech forests in Europe (van der Heijden et al., 2014). High retention coupled with efficient recycling and root uptake of atmospherically-derived Ca at Truite Rouge may therefore explain the high contribution of atmospheric deposition to wood Ca at this site.

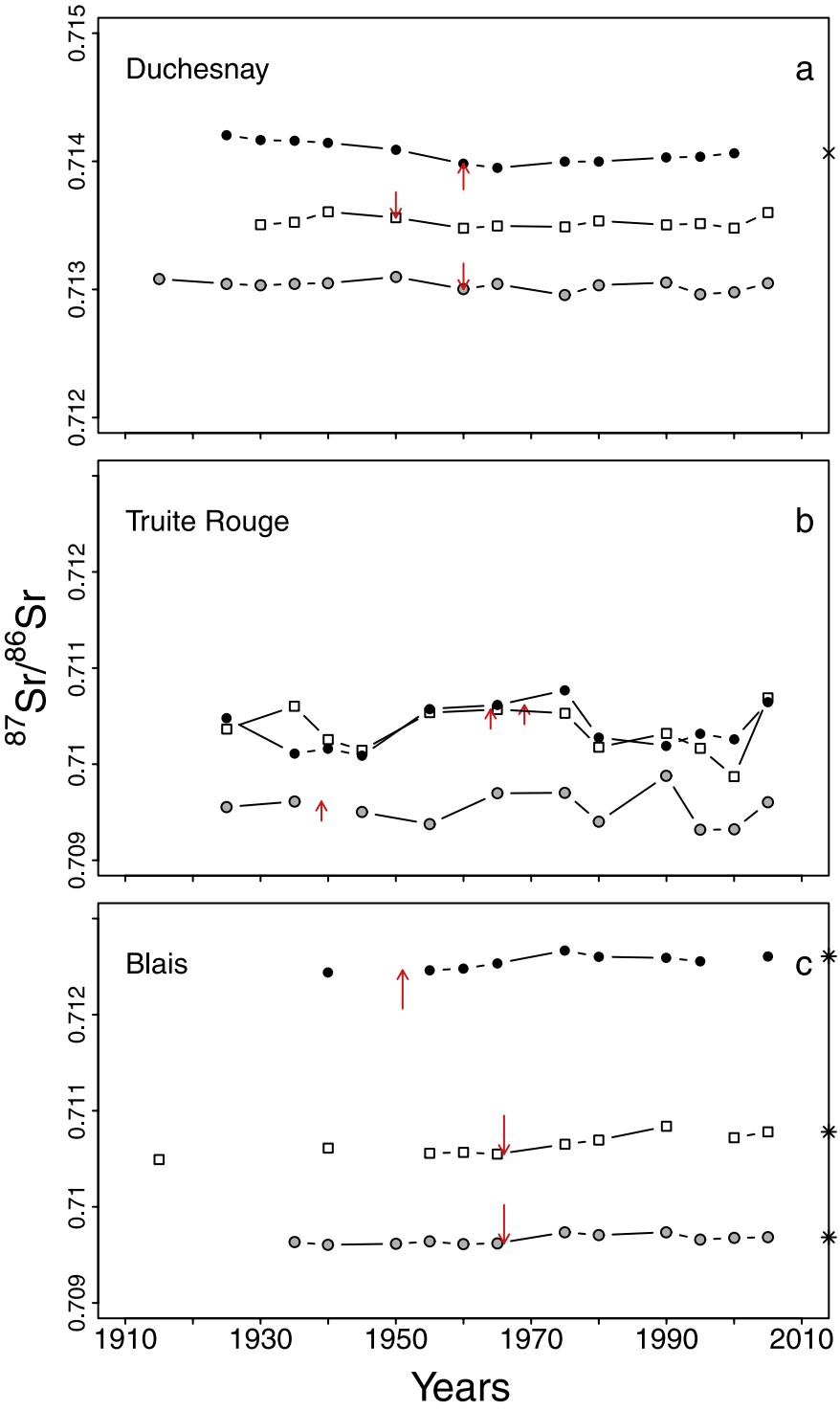

Fig. 5. $^{87}Sr/^{86}Sr$ values in the exchangeable fraction in tree rings at the Duchesnay, Truite Rouge and Blais sites. Red arrows indicate the delimitation between heartwood and sapwood for each tree. Crosses and stars in the margin indicate significant trends (Mann-Kendall test; $P < 0.01$) for the whole period and in the sapwood only, respectively. Sites are listed by increasing soil Ca availability. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4.3. Did Ca sources change over the past decades?

As previously reported for European hardwood forests affected by acidification (Drouet et al., 2005a), we initially expected an increase in the contribution of the atmospheric component to soil and wood Ca pools in the past decades, at least at the Duchesnay site where a soil mineral weathering flux and pools of Ca are much lower than at Blais and Truite Rouge. In contrast, we hypothesized that the contributions of soil mineral weathering and atmospheric deposition to soil and wood Ca would not change at Blais and Truite Rouge, given that soil weathering fluxes and soil pools of Ca are large. However, our view was challenged by the result of the mixing equation, suggesting a high contribution of the soil mineral weathering component at Duchesnay and a high contribution of the atmospheric component at Truite Rouge. The expected absence of changes at Blais was however verified. In fact, a small (<0.0004) but significant increase in $^{87}Sr/^{86}Sr$ ratio was observed for

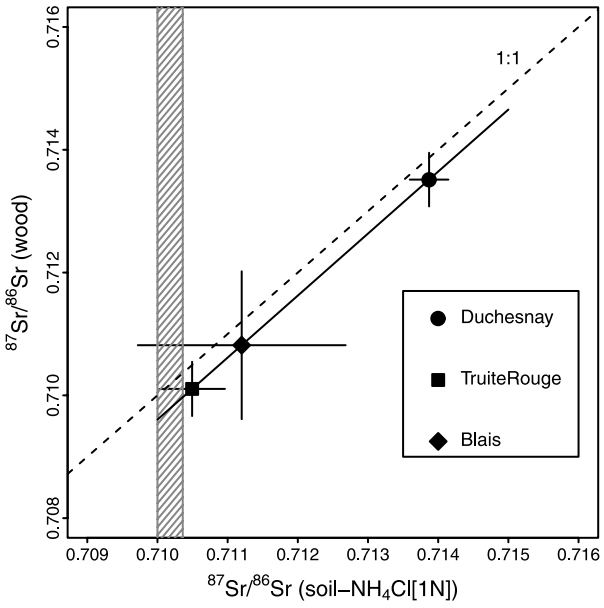

Fig. 6. Relationship between $^{87}Sr/^{86}Sr$ in wood and $^{87}Sr/^{86}Sr$ in the exchangeable fraction of the soil (NH_4Cl extraction) at the Duchesnay, Truite Rouge and Blais sites. Values are means ± SD. The grey stripe shows the range for $^{87}Sr/^{86}Sr$ of atmospheric deposition reported for the region and used in the mixing equation [(Simonetti et al., 2000; Bélanger et al., 2012)].

each tree tested at the site (Fig. 5), which may have resulted from a slight increase in the mineral weathering flux due to higher temperature or a slight decrease in the atmospheric deposition flux. We found inconsistent temporal patterns at Truite Rouge and Duchesnay. Despite no significant trend, temporal variation in wood $^{87}Sr/^{86}Sr$ ratio at Truite Rouge was larger as compared to the other sites. This agrees with the estimated large contribution (83%) of the atmospheric component at this site, which can show large temporal variation in Sr isotopic signature as compared to the soil weathering products (Bélanger et al., 2012). Overall, the trends in wood $^{87}Sr/^{86}Sr$ ratio suggest that the contributions of soil mineral weathering and atmospheric deposition remained stable or showed very small changes in the last decades at the three sites, despite the strong gradient (one order of magnitude) in soil mineral weathering and pools of Ca. This result is totally surprising for the Duchesnay site, where soil Ca exchangeable pools have been strongly depleted due to acidic deposition (Houle et al., 1997). This has resulted in a severe sugar maple decline at this site (Duchesne et al., 2002) and to extremely low leaf Ca concentration (Houle et al., 2007). The absence of change in Sr isotopic composition over time is difficult to interpret. It could have resulted from an actual absence of change in Sr source over time, which is surprising at least at the Duchesnay site, or from the radial movements of recent and low $^{87}Sr/^{86}Sr$ Sr towards the heartwood, thus dampening a potential increase in atmospheric contribution (with low $^{87}Sr/^{86}Sr$). This absence of trend differs from two previous studies where significant decreases $^{87}Sr/^{86}Sr$ in tree rings were interpreted as changes in the contribution of Ca sources over time (Drouet et al., 2005a; Bullen and Bailey 2005). It must be noted that the most important $^{87}Sr/^{86}Sr$ changes in these studies were observed between the years 1880 and 1920 while our tree ring record spans from ~1920 to 2010, which however, includes the peak of acidic deposition in the region, which occurred in the early 1980's (Houle et al., 2020; Marty et al., 2020). This factor may have also contributed to this difference.

Finally, one surprising finding in our study is that there was no significant difference in $^{87}Sr/^{86}Sr$ between the exchangeable and residual fractions of the wood (Fig. 4), which to our knowledge, is the first observation for Sr isotopes. It should be noted that the subset of samples used for this comparison originated from the three sites and from the heartwood and sapwood portions of the stem. One plausible explanation for this is the absence of changes in the Sr sources over time, meaning that the $^{87}Sr/^{86}Sr$ in nutrients taken up by the tree have varied slightly over time. It is not impossible that a difference would have been observed if a strong change in the $^{87}Sr/^{86}Sr$ of the soil solution had occurred during the study period. Another explanation is that there is a dynamic exchange of Sr (and most probably Ca) between the exchangeable and residual fractions of the wood. In this case, it will brings additional support to invalidate the potential use of the residual fraction as a better proxy than the total wood fraction for reconstructing temporal trends in soil base cation availability over time, as least for sugar maple. Clearly, more studies are needed to further understand those processes and how they vary for other tree species with different wood characteristics.

5. Conclusion

Variation in wood Ca concentrations among sites was consistent with Ca concentrations in the soil exchangeable fraction. Wood $^{87}Sr/^{86}Sr$ ratio significantly differed from site to site and was very close to $^{87}Sr/^{86}Sr$ ratio in the exchangeable fraction of the top mineral soil, supporting previous observations that the chemistry of this soil layer is a robust predictor of leave and wood chemical composition of sugar maple. Both Ca and Sr concentrations in the exchangeable fraction of the wood significantly decreased from pith to bark at the three sites, whereas no clear trend was found for the residual fraction of the wood, invalidating our hypothesis that the latter is a reliable proxy of past changes in soil Ca availability. In contrast with our hypothesis, wood $^{87}Sr/^{86}Sr$ ratio did not change over time at the more Ca-impoverished site (Duchesnay), reflecting an absence of significant changes in the relative contributions of the soil mineral weathering and atmospheric components to tree nutrition over time. Our attempt to estimate the relative contributions of these two components through mass balancing was however hampered by the similarity in the isotopic signatures of the two components at one site, and the difficulty to assess the isotopic signature of the soil mineral weathering products that directly interact with the roots or their associated mycorrhizal fungi. The use of the HNO_3[1N] extract as a proxy of the soil mineral weathering signal should not be a problem as long as the more refractory minerals in the soil matrix have a $^{87}Sr/^{86}Sr$ ratio similar or close to that of this extract. This was however not the case at the Duchesnay site where the $^{87}Sr/^{86}Sr$ ratio of the HNO_3[15N] fraction was much higher than all other extractants at all sites, which may have biased our mass balancing results. Overall, our study shows that the use of Ca concentrations in tree rings is a robust indicator of overall soil Ca availability between sites, but it cannot be easily used to track changes in Ca availability over time due to presumably radial movements and exchanges of Ca (and Sr) between the residual and exchangeable wood fractions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded by the Climate Change and Atmospheric Pollutants (CCAP) program of Environment Canada and Climate Change.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2020.104860.

References

Åberg, G., 1995. The use of natural strontium isotopes as tracers in environmental studies. Water Air Soil Pollut. 79, 309–322.

Augustin, F., Houle, D., Gagnon, C., Couchesne, F., 2016. Evaluation of three methods for estimating the weathering rates of base cations in forested catchments. Catena 144, 1–10.

Augustin, F., Houle, D., Gagnon, C., Couture, S., Courchesne, F., 2015. Partitioning the impact of environmental factors on lake concentrations and catchment budgets for base cations in forested ecosystems. Appl. Geochem. 53, 1–12.

Bailey, S.W., Hornbeck, J.W., Driscoll, C.T., Gaudette, H.E., 1996. Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. Water Resour. Res. 32, 707–719.

Bedel, L., Poszwa, A., van der Heijden, G., Legout, A., Aquilina, L., Ranger, J., 2016. Unexpected calcium sources in deep soil layers in low-fertility forest soils identified by strontium isotopes (Lorraine plateau, eastern France). Geoderma 264, 103–116.

Bélanger, N., Holmden, C., 2010. Influence of landscape on the apportionment of Ca nutrition in a Boreal Shield forest of Saskatchewan (Canada) using Sr-87/Sr-86 as a tracer. Can. J. Soil Sci. 90 (2), 267–288.

Bélanger, N., Holmden, C., Courchesne, F., Côté, B., Hendershot, W.H., 2012. Constraining soil mineral weathering 87Sr/86Sr for calcium apportionment studies of a deciduous forest growing on soils developed from granitoid igneous rocks. Geoderma 185–186, 84–96.

Bern, C.R., Townsend, A.R., Farmer, G.L., 2005. Unexpected dominance of parent-material strontium in a tropical forest on highly weathered soils. Ecology 86 (3), 626–632.

Bilodeau Gauthier, S., Houle, D., Gagnon, C., Côté, B., Messier, C., 2008. Extractability of elements in sugar maple xylem along a gradient of soil acidity. J. Environ. Qual. 37 (3), 871–879.

Bilodeau, Gauthier, S., Houle, D., Gagnon, C., Côté, B., Messier, C., 2011. Assessment of sugar maple tree growth in relation to the partitioning of elements in xylem along a soil acidity gradient. For. Ecol. Manag. 261 (1), 95–104.

Bondietti, E.A., Baes, C.F.I., McLaughlin, S.B., 1989. Radial trends in cation ratios in tree rings as indicators of the impact of atmospheric deposition on forests. Can. J. For. Res. 19, 586–594.

Blum, J.D., Klaue, A., Nezat, C.A., Driscoll, C.T., Johnson, C.E., Siccama, T.G., Likens, G. E., 2002. Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. Nature 417 (6890), 729–731.

Bullen, T.D., Bailey, S.W., 2005. Identifying calcium sources at an acid deposition-impacted spruce forest: a strontium isotope, alkaline earth element multi-tracer approach. Biogeochemistry 74 (1), 63–99. https://doi.org/10.1007/s10533-004-2619-z.

Capo, R.C., Stewart, B.W., Chadwick, O.A., 1998. Strontium isotopes as tracers of ecosystem processes: theory and methods. Geoderma 82, 197–225.

Chen, C.-C., Beauregard, F., Côté, B., Bélanger, N., Courchesne, F., Hendershot, W.H., 2013. Partitioning of the source of leaf calcium of American beech and sugar maple using leaf Ca/Sr ratios: a predominantly surficial but variable depth of Ca uptake. Plant Soil 373 (1–2), 229–242.

Clow, D.W., Mast, M.A., Bullen, T.D., Turk, J.T., 1997. Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an Alpine/Subalpine Watershed, Loch Vale, Colorado. Water Resour. Res. 33 (6), 1335.

Dambrine, E., Loubet, M., Vega, J.A., Lissarague, A., 1997. Localisation of mineral uptake by roots using Sr isotopes. Plant Soil 192 (1), 129–132. https://doi.org/10.1023/A:1004294820733.

Drever, J.I., Hurcomb, D.R., 1986. Neutralization of atmospheric acidity by chemical weathering in an alpine drainage basin in the north Cascade Mountains. Geology 14, 221–224.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., et al., 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. Bioscience 51, 180–198.

Drouet, T., Herbauts, J., Demaiffe, D., 2005a. Long-term records of strontium isotopic composition in tree rings suggest changes in forest calcium sources in the early 20th century. Global Change Biol. 11 (11), 1926–1940. https://doi.org/10.1111/j.1365-2486.2005.01034.x.

Drouet, T., Herbauts, J., Demaiffe, D., 2015. Influence of deep soil horizons on Ca nutrition of forest stands along a loessic soil sequence. Plant Soil 394 (1–2), 373–389.

Drouet, T., Herbauts, J., Gruber, W., Demaiffe, D., 2005b. Strontium isotope composition as a tracer of calcium sources in two forest ecosystems in Belgium. Geoderma 126 (3–4), 203–223.

Duchesne, L., Ouimet, R., Houle, D., 2002. Basal area growth of sugar maple in relations to acid deposition, stand health, and soil nutrients. J. Environ. Qual. 31, 1676–1683.

Duchesne, L., Ouimet, R., Morneau, C., 2003. Assessment of sugar maple health based on basal area growth pattern. Can. J. For. Res. 33, 2074–2080.

Federer, C.A., Hornbeck, J.W., Tritton, L.M., Martin, C.W., Pierce, R.S., Smith, C.T., 1989. Long-term depletion of calcium and other nutrients in eastern US forests. Environ. Manag. 13 (5), 593–601.

Galloway, J.N., Norton, S.A., Church, M.R., 1983. Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model. Environ. Sci. Technol. 17, 541A–545A.

Hajj, F., Poszwa, A., Bouchez, J., Guérold, F., 2017. Radiogenic and "stable" strontium isotopes in provenance studies: a review and first results on archaeological wood from shipwrecks. J. Archaeol. Sci. 86 (Suppl. C), 24–49. https://doi.org/10.1016/j.jas.2017.09.005.

Herbauts, J., Penninckx, V., Gruber, W., Meerts, P., 2002. Radial variations in cation exchange capacity and base saturation in the wood of pedunculate oak and European beech. Can. J. For. Res. 32, 1829–1837.

Holmden, C., Bélanger, N., 2010. Ca isotope cycling in a forested ecosystem. Geochem. Cosmochim. Acta 74, 995–1015.

Houle, D., Lamoureux, P., Bélanger, N., Bouchard, M., Gagnon, C., Couture, S., Bouffard, A., 2012. Soil weathering rates in 21 catchments of the Canadian Shield. Hydrol. Earth Syst. Sci. 16, 685–697.

Houle, D., Ouimet, R., Couture, S., Gagnon, C., 2006. Base cation reservoirs in soil control the buffering capacity of lakes in forested catchments. Can. J. Fish. Aquat. Sci. 63 (3), 471–474. https://doi.org/10.1139/f06-007.

Houle, D., Paquin, R., Camiré, C., Ouimet, R., Duschesne, L., 1997. Response of the lake clair watershed (Duchesnay, Quebec) to changes in precipitation chemistry (1988-1994). Can. J. For. Res. 27, 1813–1821.

Houle, D., Tremblay, S., Ouimet, R., 2007. Foliar and wood chemistry of sugar maple along a gradient of soil acidity and stand health. Plant Soil 300, 173–183.

Houle, D., Khadra, M., Marty, C., Couture, S., 2020. Influence of hydro-morphologic variables of forested catchments on the increase in DOC concentration in 36 temperate lakes of eastern Canada. Sci. Total Environ. 747, 141539. https://doi.org/10.1016/j.scitotenv.2020.141539.

Hunova, I., Santroch, J., Ostatnicka, J., 2004. Ambient air quality and deposition trends at rural stations in the Czech Republic during 1993- 200., Atmos. Environ. Times 38, 887–898.

Huntington, T.G., 2000. The potential for calcium depletion in forest ecosystems of southeastern United States: review and analysis. Global Biogeochem. Cycles 14, 623–638.

Hynicka, J.D., Pett-Ridge, J.C., Perakis, S.S., 2016. Nitrogen enrichment regulates calcium sources in forests. Global Change Biol. 22 (12), 4067–4079.

Jacobson, A.D., Blum, J.D., Chamberlain, C.P., Poage, M.A., Sloan, V.F., 2002. Ca/Sr and Sr isotope systematics of a Himalayan glacial chronosequence: carbonate versus silicate weathering rates as a function of landscape surface age. Geochem. Cosmochim. Acta 66, 13–27.

Kennedy, M.J., Chadwick, O.A., Vitousek, P.M., Derry, L.A., Hendricks, D.M., 1998. Changing sources of base cations during ecosystem development, Hawaiian Islands. Geology 26, 1015–1018.

Marty, C., Houle, D., Gagnon, C., 2015. Variation in stocks and distribution of organic C in soils across 21 eastern Canadian temperate and boreal forests. For. Ecol. Manag. 345, 29–38.

Marty, C., Pornon, A., Lamaze, T., Viers, J., 2014. Calcium and potassium dynamics and biopurification in two populations of the subalpine evergreen shrub Rhododendron ferrugineum. Proc. Int. Acad. Ecol. Environ. Sci. 4 (2), 50–61.

Marty, C., Duchesne, L., Couture, S., Gagnon, C., Houle, D., 2020. Effects of climate and atmospheric deposition on a boreal lake chemistry: a synthesis of 36 years of monitoring data. Sci. Total Environ. (in press).

Momoshima, N., Bondietti, E.A., 1990. Cation binding in wood: applications to understanding historical changes in divalent cation availability to red spruce. J. For. Res. 20, 1840–1849.

Nezat, C.A., Blum, J.D., Yanai, R.D., Hamburg, S.P., 2007. A sequential extraction to determine the distribution of apatite in granitoid soil mineral pools with application to weathering at the Hubbard Brook Experimental Forest, NH, USA. Appl. Geochem. 22 (11), 2406–2421. https://doi.org/10.1016/j.apgeochem.2007.06.012.

Oliva, P., Dupré, B., Martin, F., Viers, J., 2004. The role of trace minerals in chemical weathering in a high-elevation granitic watershed (Estibère, France): chemical and mineralogical evidence. Geochem. Cosmochim. Acta 68, 2223–2244.

Ouimet, Rock, Duchesne, Louis, 2005. Base cation mineral weathering and total release rates from soils in three calibrated forest watersheds on the Canadian Boreal Shield. Can. J. Soil Sci. 85, 245–260.

Perakis, S.S., Maguire, D.A., Bullen, T.D., Cromack, K., Waring, R.H., Boyle, J.R., 2006. Coupled nitrogen and calcium cycles in forests of the Oregon Coast Range. Ecosystems 9, 63–74.

Poszwa, A., Dambrine, E., Pollier, B., Atteia, O., 2000. A comparison between Ca and Sr cycling in forest ecosystems. Plant Soil 225 (1–2), 299–310.

Poszwa, A., Ferry, B., Pollie, B., Grimaldi, C., Pierre, C.-D., Loubet, M., Dambrine, E., 2009. Variations of plant and soil $^{87}Sr/^{86}Sr$ along the slope of a tropical inselberg. Ann. For. Sci. 66, 1–13.

R Development Core Team, 2015. In: R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org.

Simonetti, A., Gariépy, C., Carignan, J., 2000. Pb and Sr isotopic compositions of snowpack from Quebec, Canada: inferences on the sources and deposition budgets of atmospheric heavy metals. Geochem. Cosmochim. Acta 64 (1), 5–20.

Soil Classification Working Group, 1998. In: Canadian System of Soil Classification, third ed. https://doi.org/10.1139/9780660174044

van der Heijden, G., Legout, A., Pollier, B., Mareschal, L., Turpault, M.-P., Ranger, J., Dambrine, E., 2013. Assessing Mg and Ca depletion from broadleaf forest soils and potential causes – a case study in the Morvan Mountains. For. Ecol. Manag. 293, 65–78. https://doi.org/10.1016/j.foreco.2012.12.045.

van der Heijden, G., Legout, A., Pollier, B., Ranger, J., Dambrine, E., 2014. The dynamics of calcium and magnesium inputs by throughfall in a forest ecosystem on base poor soil are very slow and conservative: evidence from an isotopic tracing experiment (^{26}Mg and ^{44}Ca). Biogeochemistry 118 (1–3), 413–442.

Van Schöll, L., Smits, M.M., Hoffland, E., 2006. Ectomycorrhizal weathering of the soil minerals muscovite and hornblende. New Phytol. 171 (4), 805–814. https://doi.org/10.1111/j.1469-8137.2006.01790.x.

Vitousek, P.M., Kennedy, M.J., Derry, L.A., Chadwick, O.A., 1999. Weathering versus atmospheric sources of strontium in ecosystems on young volcanic soils. Oecologia 121, 255–259.

Watmough, S., 2018. An assessment of the Ca weathering sources to surface waters on the Precambrian Shield in central Ontario. Sci. Total Environ. 626, 69–76.

White, P.J., Broadley, M.R., 2003. Calcium in plants. Ann. Bot. 92 (4), 487–511.